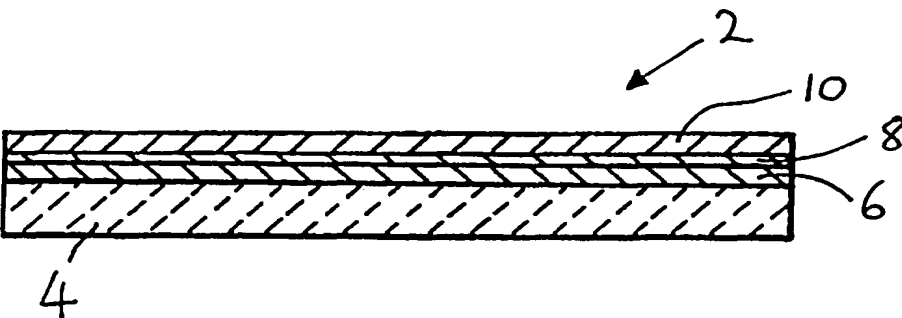


PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C03C 17/36</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/32530</b> <b>(43) International Publication Date:</b> 8 June 2000 (08.06.00)
<b>(21) International Application Number:</b> PCT/GB99/03984 <b>(22) International Filing Date:</b> 30 November 1999 (30.11.99) <b>(30) Priority Data:</b> 9826293.4 1 December 1998 (01.12.98) GB <b>(71) Applicant (for all designated States except US):</b> PILKINGTON PLC [GB/GB]; Prescott Road, St. Helens, Merseyside WA10 3TT (GB). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> GALLEGO, Jose, Manuel [GB/GB]; 22 Ellerbrook Drive, Lathom, Ormskirk, Lancashire L40 5SZ (GB). <b>(74) Agents:</b> HALLIWELL, Anthony, Charles et al.; Group Intellectual Property Dept., Pilkington plc, Pilkington European Technical Centre, Hall Lane, Lathom, Ormskirk, Lancashire L40 5UF (GB).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> IMPROVEMENTS IN COATING GLASS    <b>(57) Abstract</b> <p>A process for the production of a heat-treatable low emissivity coated glass that comprises the steps of depositing an underlayer onto a glass substrate and subsequently depositing a reflective metal layer by a vacuum deposition process, wherein the underlayer is deposited by a pyrolytic deposition process. Preferably an anti-reflection layer is deposited by a vacuum deposition process on to the coated glass after deposition of the reflective metal layer. The underlayer may comprise a silicon oxide, the reflective metal layer may comprise silver and the anti-reflection layer may comprise a metal oxide, especially tin oxide or zinc oxide. The coated glass preferably has an emissivity of below 0.2 after heat treatment in an oxidising atmosphere.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

### Improvements in Coating Glass.

This invention relates to a process for the production of a heat-treatable low emissivity coated glass and to a heat-treatable low emissivity coated glass.

It is known that transparent glass substrates with a thin reflective metal coating, typically silver 5 nm to 30 nm thick, may be produced with low emissivity and a high visible light transmission i.e. which reflect a high proportion of infra-red radiation incident upon them but allow visible radiation to pass through. The use of such coatings on window glass leads to a reduction in heat loss. For optimum light transmission, the silver layers are sandwiched between thin anti-reflection layers of metal oxide. Such low emissivity coatings are produced by vacuum deposition processes, especially sputtering, and normally comprise a thin layer of silver sandwiched between two layers of metal oxide. Such coatings are described, for example, in UK patent specification GB 2 129 831.

Unfortunately, such low emissivity coatings are not stable to heating in air, and the coating loses its properties of low emissivity and high light transmission when the coated glass is subjected to a thermal cycle which cycle is required for bending or toughening the glass. To obtain a toughened or bent glass substrate bearing a low emissivity reflective metal coating that has high light transmission it has been necessary to either bend and/or toughen the glass before depositing the reflective metal coating or to deposit an additional, protective layer over the reflective metal layer before bending/toughening. GB patent 2 186 001B describes this problem and a process for the production of a bent and/or toughened silver coated glass substrate wherein an additional metal layer of aluminium, titanium, zinc or tantalum is deposited over the silver layer. The additional metal layer protects the silver layer beneath it from degradation during the bending or toughening thermal cycle by acting as a barrier layer between the silver layer and the oxidising atmosphere.

The applicants have now discovered that the above problem may be alleviated by depositing an underlayer onto a glass substrate using a pyrolytic deposition process and subsequently depositing a reflective metal layer onto the coated substrate.

According to one aspect of the present invention there is provided a process for the production of a heat-treatable low emissivity coated glass that comprises the steps of

- a) depositing an underlayer onto a glass substrate, and
- b) subsequently depositing a reflective metal layer by a vacuum deposition method, characterised in that the underlayer is deposited by a pyrolytic deposition process.

Surprisingly, the underlayer deposited by a pyrolytic deposition process provides protection to the reflective metal layer on heat-treatment despite its position *underneath* the reflective metal layer. In preferred embodiments of the invention a barrier layer is unnecessary which is advantageous because then fewer layers need be deposited reducing the time needed for the process and so increasing production rates.

Normal emissivity is defined in International Standard ISO 12092:1994 (F), Annex A as  $\epsilon_N = 1 - R_N$  where  $R_N$  is the normal reflectance over the wavelength range 5.5  $\mu\text{m}$  to 50  $\mu\text{m}$  at 283 K. Low emissivity coatings as discussed herein are those which have a normal emissivity of below about 0.4. The lower the emissivity of the coated glass the better are the heat rejecting properties of the glass.

Usually, the reflective metal layer is deposited directly on the underlayer, but one or more intermediate layers (e.g. of metal oxide) may be deposited between the underlayer and the reflective metal layer if, for example it is desired to deposit an anti-reflection layer or anti-reflection layers additional to the underlayer. Layers may also be deposited beneath the underlayer.

Pyrolytic deposition processes are processes which are usually carried out at substantially atmospheric pressure wherein a fluid is directed onto a hot substrate under conditions such that a coating is formed on the substrate. Processes wherein the fluid is a liquid are termed spray deposition processes and processes wherein the fluid is a vapour are termed chemical vapour deposition (CVD) processes. The preferred pyrolytic deposition process for deposition of the underlayer is CVD because it may be performed on line (i.e. during the float glass production process) and produces good quality coating layers.

It is thought that any pyrolytically deposited material could be advantageously used as an underlayer in the present invention. For example, the underlayer may comprise silicon oxide, silicon oxide containing carbon (often referred to as silicon oxycarbide and which may be deposited as described in European patent application 275 662 A), silicon oxide containing nitrogen (often referred to as silicon oxynitride and which may be deposited as described in GB patent 2 031 756 B), titanium oxide, tin oxide, titanium nitride, silicon nitride, silicon carbide, silicon or a mixture comprising one or more of these materials. The preferred underlayer comprises a silicon oxide, especially a silicon oxide containing carbon, because silicon oxide layers are relatively easily deposited by CVD in a range of stoichiometries (and hence a range of refractive indices).

If silicon oxide is selected as the underlayer material, pyrolytically depositing the underlayer preferably comprises contacting the glass substrate with a fluid mixture containing a silicon source, an oxygen source and a carbon source under conditions such that a silicon oxide layer, preferably containing carbon, is deposited. Preferably, the fluid mixture is a vapour mixture.

The underlayer will usually be deposited on the glass substrate when the glass substrate is at a temperature in the range 450°C to 800°C, especially when the glass substrate is at a temperature in the range 600°C to 780°C.

Preferably, the underlayer is deposited on to a glass ribbon during the float glass production process at substantially atmospheric pressure in which case the glass ribbon will usually be cut into sheets after deposition of the underlayer (and before deposition of other layers including the reflective metal and any subsequent layers) for storage or convenient transport from the float glass production facility to the vacuum deposition facility.

The reflective metal layer may comprise silver or aluminium, preferably silver.

A vacuum deposition process is one which is usually performed at a pressure of lower than about 0.1 mbar and includes such methods as sputtering, reactive sputtering, evaporation and other forms of physical vapour deposition. The preferred vacuum deposition method for depositing a reflective metal layer is sputtering.

Usually, an anti-reflection layer is deposited by a vacuum deposition process on to the coated glass after deposition of the reflective metal layer. Preferably, the anti-reflection layer comprises a metal oxide, more preferably the anti-reflection layer comprises zinc oxide or tin oxide. More than one anti-reflection layer may be deposited.

If an anti-reflection layer is deposited by reactive sputtering in an oxidising atmosphere comprising, for example, more than 70% by volume oxygen, a further protective layer is preferably deposited on the reflective metal layer before the sputtering step so as to protect the reflective metal layer from degradation by the oxidising atmosphere. The further protective layer preferably comprises inconel or nichrome. Other layers may also be deposited between the reflective metal layer and anti-reflection layer(s).

The invention also provides a process for the production of coated glass having a coating with more than one reflective metal layer. Thus, in an embodiment of the invention a second reflective metal layer and a second anti-reflection layer are sequentially deposited by a vacuum deposition process after deposition of the first anti-reflection layer. In this

embodiment of the invention (where the coated glass has two reflective metal layers) the glass will usually have lower emissivity than in the single reflective metal layer embodiment and also, with appropriate layer thicknesses, a reduced transmission of solar heat.

The process may additionally comprise a heat treatment step wherein the heat-treatable low emissivity coated glass is subjected to a temperature in the range 400°C to 750°C in an oxidising atmosphere, which is usually directed to the production of bent and/or toughened coated glass. Surprisingly and advantageously, the visible transmission of the heat-treatable low emissivity coated glass may be increased by the heat-treatment step.

In a further aspect, the invention provides a heat-treatable low emissivity coated glass comprising a glass substrate having a multilayer coating on a surface, said multilayer coating comprising a pyrolytically deposited underlayer, a vacuum deposited reflective metal layer and a vacuum deposited anti-reflection layer.

Preferably the underlayer comprises a silicon oxide, more preferable a silicon oxide containing carbon and advantageously, the underlayer will have a refractive index in the range 1.5 to 3 because an underlayer with a refractive index in this range enables a coating with a low visible light reflection to be produced (i.e. this range of refractive index is suitable for an anti-reflection underlayer). In most embodiments of the invention the underlayer has a thickness in the range 30 to 100 nm.

The reflective metal layer usually comprises silver or aluminium and preferably has a thickness in the range 5 to 30 nm, more preferably in the range 7 to 18 nm. At thicknesses lower than 7 nm the reflective metal layer may be discontinuous (this results from the growth mechanism of a layer and may occur even on a flat substrate) and will then not possess the properties of the bulk metal (resulting in poor infra red reflecting properties), whereas thicknesses higher than 18 nm may cause the coated glass to have too high a reflectivity to visible light.

The anti-reflection layer beneficially has a thickness in the range 30 nm to 90 nm.

Coated glass according to the invention will usually have a normal emissivity of below 0.2, preferably below 0.1. Coated glass according to the invention which has been heat treated by heating it to a temperature in the range 400 to 700°C in an oxidising atmosphere will usually have a normal emissivity of below 0.2, preferably below 0.1, after the heat treatment step. Surprisingly and advantageously, heat treatment tends to reduce the emissivity of those embodiments of the invention having a single reflective metal layer.

It is thought that a pyrolytically deposited underlayer reduces oxygen induced degradation during heat treatment in an oxidising atmosphere by scavenging oxygen that would otherwise attack the silver layer. Underlayers that scavenge oxygen deposited using methods other than pyrolysis may also be useful as underlayers in the invention.

Thus, in a further aspect of the present invention a heat-treatable low emissivity coated glass comprises a glass substrate having a multilayer coating on one surface, said multilayer coating comprising an oxygen scavenging underlayer, a vacuum deposited reflective metal layer and a vacuum deposited anti-reflection layer.

The oxygen scavenging underlayer may comprise a material deficient in oxygen that has the potential to bind oxygen in preference to the reflective metal layer (usually a silver layer). An example of a material likely to be suitable as an oxygen scavenging underlayer is oxygen deficient silicon oxide ( $\text{SiO}_x$  where  $x$  is less than 2).

Coated glasses produced by the process of the present invention have uses in many areas of glass use including as a glazing pane in a multiple glazing unit or as a glazing pane in a laminated glass which will also comprise a polymer interlayer (usually of polyvinylbutyral) and a second glazing pane.

So that the invention may be better understood reference will now be made to the following drawings in which:-

Figure 1 illustrates schematically a section through a coated glass having a single reflective metal layer, the coated glass produced by a process according to the invention.

Figure 2 illustrates schematically a section through a coated glass having two reflective metal layers, the coated glass produced by a process according to the invention.

Referring to Fig. 1, a low emissivity coated glass 2 with a single silver layer 8 comprises a glass substrate 4, a pyrolytically deposited underlayer 6 of silicon oxide containing carbon of thickness 58 nm, a DC magnetron vacuum sputtered silver layer 8 of thickness 12 nm and a further layer of sputtered zinc oxide 10 of thickness 38 nm. The underlayer 6 is deposited by on line chemical vapour deposition. The underlayer 6 and the zinc oxide layer 10 act as anti-reflection layers.

Referring to Fig. 2, a low emissivity coated glass 12 with two silver layers 18 and 22 comprises a glass substrate 14, a pyrolytically deposited underlayer 16 of silicon oxide containing carbon of thickness 58 nm, and DC magnetron vacuum sputtered layers of: silver 18 of thickness 8.1 nm, zinc oxide 20 of thickness 85 nm, silver 22 of thickness 8.4 nm, and

zinc oxide 24 of thickness 49 nm. A two silver layer low emissivity coating can provide greater infra red reflection compared to a single silver layer low emissivity coating and can also provide good solar control properties (i.e. reducing transmitted solar heat).

The invention is further illustrated by the following Examples, in which vacuum deposited coatings were applied to glass substrates coated with an underlayer of silicon oxide containing carbon.

The silicon oxycarbide (silicon oxide containing carbon) underlayer was deposited substantially as described in European patent application EP 0 275 662A by applying a flowing gaseous mixture to the upper surface of a glass ribbon during the float glass production process using a water-cooled graphite coater. The gaseous mixture was applied at a position where the glass temperature was approximately 773°C as the ribbon advanced at a ribbon speed of 127 m/hr over the float bath. The gaseous mixture comprised nitrogen (as carrier gas, flow rate 0.92 kg/hr), monosilane ( $\text{SiH}_4$ , flow rate 0.06 kg/hr), ethylene (flow rate 1.84 kg/hr) and carbon dioxide (flow rate 2.31 kg/hr). The gaseous mixture was caused to flow parallel to the glass surface in the direction of movement of the glass under laminar flow conditions using an apparatus as described in GB patent specification 1 507 966 extending over the 2 m width of the glass ribbon, and with a path of travel extending approximately 0.1 m down-ribbon. The thickness of the glass was about 2.8 mm.

At the end of the float line, samples of the glass coated with the underlayer were cut from the glass ribbon. Coating layers were vacuum deposited on the samples at room temperature by sputtering or reactive sputtering using an Airco Temescal ILS 1600 sputtering plant and DC magnetron sputtering using metal targets of 99.9% purity or better. Deposition conditions for layers comprising silver, inconel, tin (IV) oxide and zinc oxide are described in Table 1.

The layer materials and layer thicknesses for the underlayer and the vacuum deposited coatings in the Examples are described in Table 2.

Table 3 describes the optical properties of the coated glasses of the Examples before and after (the values after heat treatment are in brackets) heat treatment to simulate toughening. The heat treatment consisted of subjecting the coated glass to a temperature of 640°C in air for 1.5 minutes. The visible transmission, reflection and the transmission and reflection colours in Table 3 were measured using an Hitachi U400 spectrophotometer and/or a Perkin Elmer 883 spectrophotometer, and calculated using the methods described in



International Standard ISO 12092:1994 (F) and other standard methods. The thicknesses of the layers were determined by computer fitting the spectra and by profilometry (Sloan Dektak II profilometer) after appropriate etching treatment (e.g. with aqueous hydrofluoric acid).

Table 1

	Layer Material			
	Silver	Inconel	Tin Oxide	Zinc Oxide
Power Density (W/cm <sup>2</sup> )	0.61	0.36	3.6	3.8
Gas Pressure (10 <sup>-3</sup> mbar)	9.3	11.8	6.7	6.8
Gas Composition (%)				
Ar	100	100	0	30
O <sub>2</sub>	0	0	100	70
Target - Substrate Distance (cm)	11	11	11	11
Substrate speed (cm/s)	2.7	2.9	3.1	3.1
Number of passes to obtain:	8	8	10	10
Thickness (Å)	102	10	362	340

Table 2

Layers	Example 1	Example 2	Example 3	Example 4
Silicon Oxide underlayer (nm)	58	58	58	58
First Silver Layer (nm)	11.9	8.1	11.4	7.9
First Inconel Layer (nm)	-	-	0.65	0.56
First Dielectric Layer (nm)	38 (ZnO)	85 (ZnO)	42 (SnO <sub>2</sub> )	83 (SnO <sub>2</sub> )
Second Silver Layer (nm)	-	8.4	-	8.8
Second Inconel Layer (nm)	-	-	-	0.54
Second Dielectric Layer (nm)	-	49 (ZnO)	-	48 (SnO <sub>2</sub> )

Table 3

	Example 1	Example 2	Example 3	Example 4
	Value before (after) heat treatment	Value before (after) heat treatment	Value before (after) heat treatment	Value before heat treatment
Visible Transmission %	76.3 (78.2)	74.1 (74.9)	74.5 (78.1)	73.2
Visible Reflection %	9.5 (9.1)	5.4 (5.2)	10.7 (9.2)	6.4
Transmission Colour				
a*	-4.2 (-3.9)	-3.9 (-4.2)	-5.1 (-3.4)	-4.6
b*	5.3 (4.9)	5.1 (5.4)	7.2 (7.4)	6.7
L	91 (92)	88 (88)	89 (91)	86.2
Reflection Colour				
a*				
b*	8.2 (7.9)	3.1 (3.5)	10.4 (8.9)	3.4
L	-3.2 (-3.8)	2.5 (3.2)	-5.3 (-4.8)	5.5
	35.2 (33.5)	31.2 (29.5)	38.7 (34.5)	30.2
Normal Emissivity	0.072 (0.069)	0.060 (0.065)	0.076 (0.072)	0.066

Claims

1. A process for the production of a heat-treatable low emissivity coated glass that comprises the steps of
  - a) depositing an underlayer onto a glass substrate and
  - b) subsequently depositing a reflective metal layer by a vacuum deposition method, characterised in that the underlayer is deposited by a pyrolytic deposition process.
2. A process according to claim 1 wherein the reflective metal layer is deposited directly on the underlayer.
3. A process according to either claim 1 or claim 2 wherein the underlayer comprises a silicon oxide.
4. A process according to any one of claims 1-3 wherein the underlayer comprises a silicon oxide containing carbon.
5. A process according to any one of claims 1-4 wherein the pyrolytic deposition of the underlayer comprises contacting the glass substrate with a fluid mixture containing a silicon source, an oxygen source and a carbon source under conditions such that a silicon oxide layer, preferably containing carbon, is deposited.
6. A process according to claim 5 wherein the fluid mixture is a vapour mixture.
7. A process according to any one of claims 1-3 wherein the underlayer comprises silicon oxide containing nitrogen.
8. A process according to any one of the preceding claims wherein the underlayer is deposited on the glass substrate when the glass substrate is at a temperature in the range 450°C to 800°C.

9. A process according to claim 8 wherein the underlayer is deposited on the glass substrate when the glass substrate is at a temperature in the range 600°C to 780°C
10. A process according to any one of preceding claims wherein the underlayer is deposited on to a glass ribbon during the float glass production process at substantially atmospheric pressure.
11. A process according to claim 10 wherein the glass ribbon is cut into sheets after deposition of the underlayer.
12. A process according to any one of the preceding claims wherein the reflective metal layer comprises silver or aluminium.
13. A process according to any one of the preceding claims wherein an anti-reflection layer is deposited by a vacuum deposition process on to the coated glass after deposition of the reflective metal layer.
14. A process according to claim 13 wherein the anti-reflection layer comprises a metal oxide.
15. A process according to claim 14 wherein the anti-reflection layer comprises zinc oxide or tin oxide.
16. A process according to any one of claims 13-15 wherein a second reflective metal layer and a second anti-reflection layer are sequentially deposited by a vacuum deposition process after deposition of the first anti-reflection layer.
17. A process according to any one of the preceding claims additionally comprising a heat treatment step wherein the heat-treatable low emissivity coated glass is subjected to a temperature in the range 400 to 750°C in an oxidising atmosphere.

18. A process according to claim 17 wherein the heat treatment step is directed to the production of bent and/or toughened coated glass.
19. A process according to either claim 17 or claim 18 wherein the visible transmission of the coated glass is increased by the heat-treatment step.
20. A coated glass produced by a process according to any one of the preceding claims.
21. A heat-treatable low emissivity coated glass comprising a glass substrate having a multilayer coating on one surface, said multilayer coating comprising a pyrolytically deposited underlayer, a vacuum deposited reflective metal layer and a vacuum deposited anti-reflection layer.
22. A coated glass according to claim 21 wherein the underlayer comprises a silicon oxide.
23. A coated glass according to claim 22 wherein the underlayer comprises a silicon oxide containing carbon.
24. A coated glass according to any one of claims 21-23 wherein the underlayer has a refractive index in the range 1.5 to 3.
25. A coated glass according to any one of claims 21-24 wherein the underlayer has a thickness in the range 30 to 100 nm.
26. A coated glass according to any one of claims 21-25 wherein the reflective metal layer has a thickness in the range 5 to 30 nm.
27. A coated glass according to claim 26 wherein the reflective metal layer has a thickness in the range 7 to 18 nm.
28. A coated glass according to any one of claims 21-27 wherein the anti-reflection layer has a thickness in the range 30 nm to 90 nm.

29. A coated glass according to any one of claims 21-28 wherein the coated glass has a normal emissivity of below 0.2.
30. A coated glass according to any one of claims 21-29 wherein the coated glass has a normal emissivity of below 0.1.
31. A coated glass according to any one of claims 21-30 wherein the coated glass has been heat treated by heating it to a temperature in the range 400 to 700°C in an oxidising atmosphere.
32. A coated glass according to claim 31 wherein the coated glass has a normal emissivity of below 0.2 after the heat treatment step.
33. A coated glass according to claim 32 wherein the coated glass has a normal emissivity of below 0.1 after the heat treatment step.
34. A heat-treatable low emissivity coated glass comprising a glass substrate having a multilayer coating on one surface, said multilayer coating comprising an oxygen scavenging underlayer, a vacuum deposited reflective metal layer and a vacuum deposited anti-reflection layer.
35. A multiple glazing unit comprising a first glazing pane of a coated glass according to claim 34 and a second glazing pane.
36. Laminated glass comprising a first glazing pane of a coated glass according to claim 34, an interlayer and a second glazing pane.
37. A process for producing coated glass substantially as herein described with particular reference to the Examples 1-4.

Fig.1.

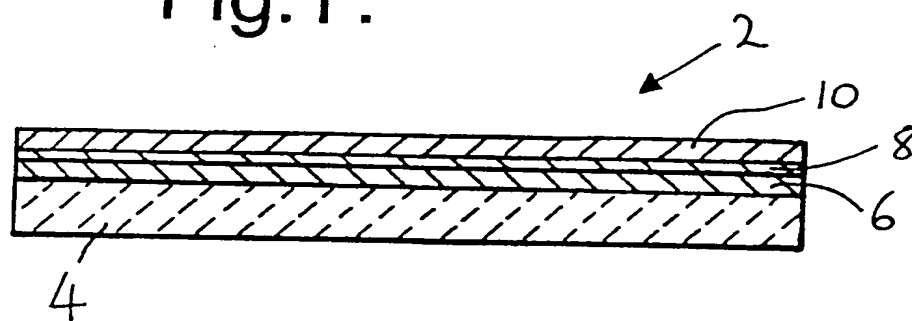
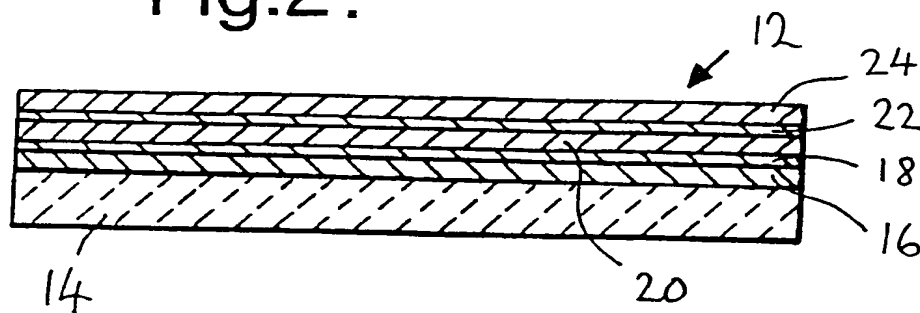


Fig.2.





# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/03984

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C03C17/36

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 275 662 A (PILKINGTON PLC) 27 July 1988 (1988-07-27) cited in the application claims	1-37
Y	EP 0 543 077 A (LEYBOLD AG) 26 May 1993 (1993-05-26) claims 1-11	1-37
X	DATABASE WPI Section Ch, Week 198823 Derwent Publications Ltd., London, GB; Class L01, AN 1988-158891 XP002131524 & JP 63 100043 A (NIPPON SHEET GLASS CO LTD), 2 May 1988 (1988-05-02) abstract	1-4

-/-

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

6 March 2000

Date of mailing of the international search report

13/03/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Reedijk, A

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 99/03984

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 583 871 A (PILKINGTON UK LTD) 23 February 1994 (1994-02-23) page 5, line 26 - line 58	1-37
A	CHEMICAL ABSTRACTS, vol. 115, no. 26, 30 December 1991 (1991-12-30) Columbus, Ohio, US; abstract no. 285686f, page 364; XP000373670 abstract & JP 03 126644 A (ASAHI OPTICAL CO. LTD.) 29 May 1991 (1991-05-29)	1-3

## INTERNATIONAL SEARCH REPORT

information on patent family members

Inter. Application No

PCT/GB 99/03984

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0275662	A	27-07-1988	AT 58114 T	15-11-1990
			AU 593966 B	22-02-1990
			AU 8288587 A	30-06-1988
			CA 1327143 A	22-02-1994
			CN 1018636 B	14-10-1992
			CS 8709789 A	12-09-1990
			DD 264911 A	15-02-1989
			DK 685687 A	25-06-1988
			FI 875657 A,B,	25-06-1988
			GB 2199848 A,B	20-07-1988
			GR 3002521 T	25-01-1993
			IE 60946 B	07-09-1994
			IN 170516 A	04-04-1992
			JP 1201046 A	14-08-1989
			JP 1942619 C	23-06-1995
			JP 6074158 B	21-09-1994
			KR 9502332 B	16-03-1995
			MX 170772 B	14-09-1993
			NO 875344 A,B,	27-06-1988
			PT 86460 A,B	01-01-1988
			SU 1830053 A	23-07-1993
			TR 23524 A	01-03-1990
			US 4828880 A	09-05-1989
			ZA 8709553 A	16-06-1988
EP 0543077	A	26-05-1993	DE 4135701 A	13-05-1993
			DE 59204255 D	14-12-1995
			ES 2079718 T	16-01-1996
			JP 5221692 A	31-08-1993
			US 5279722 A	18-01-1994
JP 63100043	A	02-05-1988	NONE	
EP 0583871	A	23-02-1994	AT 145195 T	15-11-1996
			AU 4152993 A	13-01-1994
			BR 9302815 A	22-02-1994
			CA 2099519 A	12-01-1994
			CN 1081657 A	09-02-1994
			CZ 9301318 A	16-02-1994
			DE 69305936 D	19-12-1996
			DE 69305936 T	17-04-1997
			DK 583871 T	21-04-1997
			EG 20125 A	31-07-1997
			ES 2096864 T	16-03-1997
			FI 933164 A	12-01-1994
			GB 2268509 A,B	12-01-1994
			GR 3022231 T	30-04-1997
			HU 70362 A	30-10-1995
			IL 106202 A	31-01-1996
			JP 6183787 A	05-07-1994
			MX 9304101 A	31-01-1994
			NZ 248032 A	24-02-1995
			PL 299635 A	21-03-1994
			TR 26801 A	08-08-1994
			US 5505989 A	09-04-1996
			US 5580364 A	03-12-1996
			US 5745291 A	28-04-1998
			ZA 9304664 A	25-01-1994

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/GB 99/03984

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 3126644 A	29-05-1991	JP 1890317 C JP 6013418 B	07-12-1994 23-02-1994